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ON THE SINGLET→TRIPLET ABSORPTION IN A FEW POLYSUBSTITUTED BENZENES IN THE VAPOUR STATE*

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ABSTRACT. The absorption spectra in the near ultraviolet region of ortho-, meta- and parafluorotoluene, *m*-chlorotoluene, 2, 4-dichlorotoluene and 3, 4-dichlorotoluene in the vapour state at the room temperature and with a path length equivalent to about 7 mm of the liquids have been investigated and compared with those due to equivalent path lengths of the liquids. In the case of 2, 4-dichlorotoluene and 3, 4-dichlorotoluene the spectra have also been photographed with the vapours at about 205°C using a high dispersion spectrograph.

It has been observed that these vapours exhibit continuous absorption starting at different points in the region lying between 26000 cm^{-1} and 32000 cm^{-1} and increasing towards longer wavelengths. When the vapours are liquefied the region of absorption shifts towards longer wavelengths, the shift being larger for ortho compounds than for the para compounds, but the long wavelength limit in the spectra of the isomeric molecules in liquid state are almost identical. It has been found that the spectra due to the vapours at different temperatures are identical. These results have been discussed.

INTRODUCTION

The absorption spectra of some substituted benzene and toluene compounds in the vapour state at the saturation vapour pressure of the substances at the room temperature and with a path length of about 18.90 metres were studied recently by Sirkar and Roy (1960) and by Roy (1961). They observed weak continuous structureless absorption spectrum in the near ultraviolet region at large distances on the long wavelength side of the region of absorption due to singlet→singlet transition. They assigned this continuous absorption to singlet→triplet transition in the molecules. It was further observed that the continuous absorption increases considerably in some cases when equivalent path lengths of the substances in the liquid state are used. It was concluded that the increase is due to perturbation by the surrounding molecules of the same kind in the liquid state.

In the previous experiments long path of the vapours at low pressures at the room temperature was used in order to obtain sufficient path lengths of the vapour equivalent to that of the liquid without change of temperature. It was not known whether the continuous absorption spectrum attributed to singlet→triplet transi-

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tion in the molecules is affected by temperature and pressure. It was, therefore, thought worthwhile to study the influence of temperature on the absorption due to the vapour. For this purpose the absorption spectra in the near ultraviolet region in two dihalogen substituted toluenes in the vapour state at the saturation pressures at the boiling points of the liquids and with path lengths of 140 cm have been investigated and compared with those due to equivalent path lengths of the substances in the vapour and liquid states at the room temperature.

The influence of heavy atoms as substituents in the benzene or naphthalene molecule on the singlet→triplet absorption spectrum was investigated by previous authors (McClure, Blake and Hanst, 1954) but it was not definitely known how such an influence changes with the change in position of the substituents in the ring. To find out such changes the absorption spectra of a few halogen substituted toluenes in the vapour state at the saturation pressures at the room temperature have been investigated using a path length about 18.90 metres and compared with the spectra due to the liquids with equivalent path lengths.

EXPERIMENTAL

The substances selected for the present investigation are ortho-, meta- and parafluorotoluene, metachlorotoluene, 2-,4-dichlorotoluene and 3, 4-dichlorotoluene. Orthofluorotoluene of chemically pure quality was obtained from Dr. Theodor Schuchardt, Germany, meta- and parafluorotoluene from Eastman Kodak Co., U.S.A. and metachlorotoluene, 2,4-dichlorotoluene and 3, 4-dichlorotoluene from Fisher Scientific Company, U.S.A. The colourless samples were distilled several times under reduced pressure before being used in the present investigation.

The experimental arrangement for recording the ultraviolet absorption spectra of the substances at the room temperature was the same as that employed in the previous investigations (Sirkar and Roy, 1960; Roy, 1961). The absorption spectra of the substances in the vapour state where photographed first by filling the 18.90 metres long absorption cell with the vapours of the compounds at the saturation pressures at about 24°C. The pressures measured with a differential manometer were found to be about 60 mm, 50 mm and 45 mm of Hg in the cases of the fluorotoluenes, metachlorotoluene and dihalogenated toluenes respectively. The equivalent path lengths of the liquids were 7.4 mm, 6.5 mm and 6.4 mm respectively. In each case an empty cell of length equal to equivalent path length for the liquid was first placed in the path of the beam while the absorption spectrum due to the vapour was recorded with a cell of length 1890 cm. The long cell was then evacuated and the short cell was filled with the pure liquid and the absorption spectrum of the liquid was photographed by the side of the spectrum due to the vapour. An Adam Hilger medium quartz spectrograph giving a dispersion of about 22 A/mm in the 3500 A region was used for this purpose.

The absorption spectra of the substances in the vapour state at temperatures near about the boiling points of the liquids were studied in the cases of 2, 4-dichlorotoluene and 3,4-dichlorotoluene using a 140 cm long Pyrex glass cell fitted with quartz windows. The cell was placed inside a long cylindrical heater and was heated to a temperature slightly above the boiling point of the liquid and another heater was used to heat the liquid contained in a bulb attached through a side tube to the long cell. The temperature of the bulb was raised to the boiling point of the liquid and was kept constant during the experiment. The corresponding path length for the liquid was 7.6 mm in each case. After photographing the absorption spectrum of the vapour, that due to the liquid at the room temperature was photographed on the same film using a cell 7.6 mm long and the same time of exposure. The continuous spectrum due to the incident light was also photographed in order to compare the absorption spectrum of the vapour with the spectrum of the incident light. A Hilger E. 476 automatic quartz spectrograph giving a dispersion of about 8 A/mm in the 3500 A region was used for photographing the spectra of the vapours at high temperature (205°C). Agfa Isopan films backed by metal plates were used to photograph the spectra. Iron arc spectrum was photographed on each spectrogram as comparison. Microphotometric records of the spectrograms were obtained with a self-recording microphotometer made by Kipp and Zonen. The wave lengths in the continuous absorption spectra were measured by drawing a sharp line across the spectrogram in the position of a known iron line in the adjacent iron arc spectrum and comparing the microphotometric record of the iron arc spectrum with that of the absorption spectrum.

RESULTS AND DISCUSSION

The microphotometric records of the absorption spectra due to pure orthofluorotoluene and parafluorotoluene in the liquid and vapour states at room temperature are reproduced in Figs. 1(a)–1(d), those due to pure 2, 4- and 3, 4-dichlorotoluene are reproduced in Figs. 2(a)–2(d). The records due to pure *m*-fluorotoluene and *m*-chlorotoluene are reproduced in Figs. 3(a)–3(d) respectively. The microphotometric records of the absorption spectra due to pure 2, 4- and 3, 4-dichlorotoluene at the high temperature are shown in Figs. 4(a), (b) and 5(a), (b) respectively. The reference line in the records has the wave length 4046A.

It can be seen from Figs. 1, 2, 3 and 4 that the vapours of the substances show continuous absorption in the region 3600 A–3300A and its strength increases rapidly towards shorter wavelengths starting from the long wavelength limit. The position of the long wavelength limit is slightly different for the different compounds. Also the relative positions of the substituents has some influence on the strength of the S→T absorption, as can be seen from a comparison of the records due to ortho- and parafluorotoluene in Figs. 1(a), 1(b), 1(c) and 1(d) and those due to 2, 4-dichlorotoluene and 3, 4-dichlorotoluene shown in Figs. 2(a), 2(b), 2(c) and 2(d). It appears that in the vapour state the strength of absorption

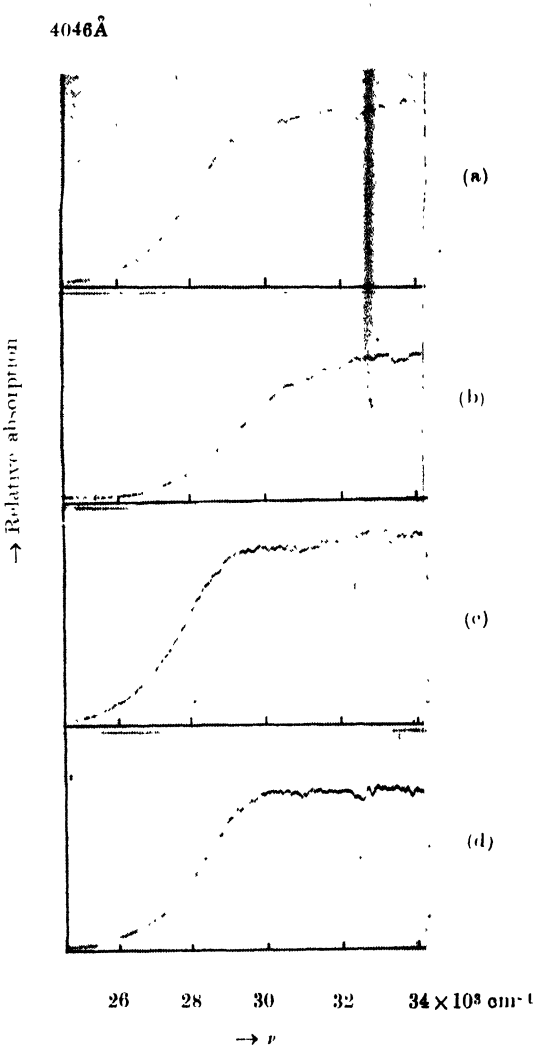

Fig. 1 (a) *o*-Fluorotoluene (liquid)
(b) *o*-Fluorotoluene (vapour)
(c) *p*-Fluorotoluene (liquid)
(d) *p*-Fluorotoluene (vapour)

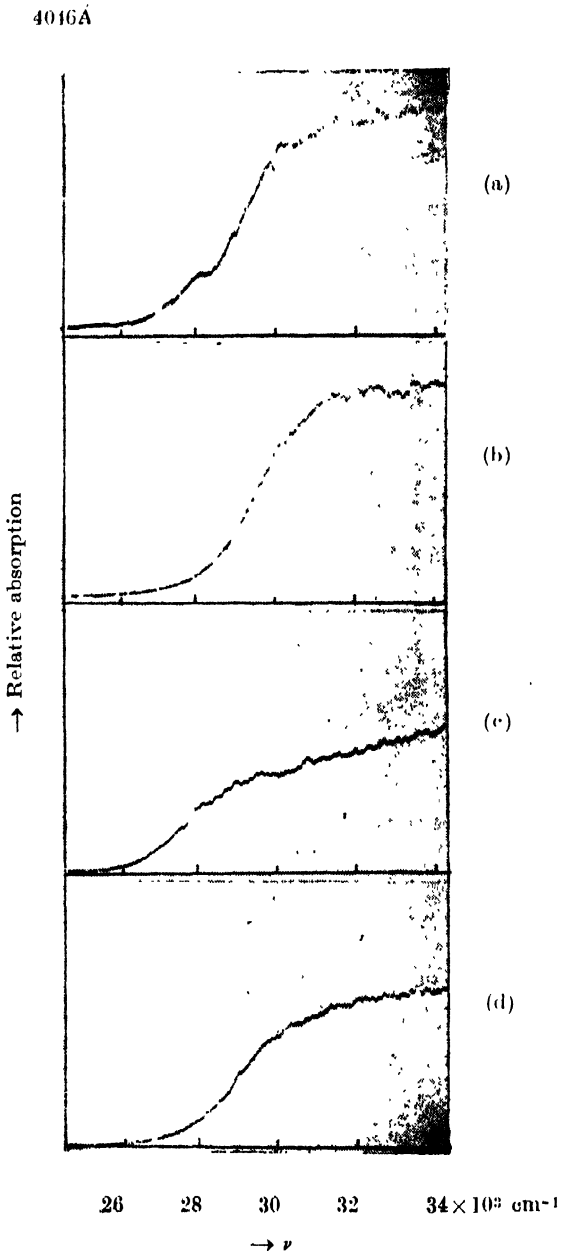

Fig. 2 (a) 2,4-Dichlorotoluene (liquid)
(b) 2,4-Dichlorotoluene (vapour)
(c) 3,4-Dichlorotoluene (liquid)
(d) 3,4-Dichlorotoluene (vapour)

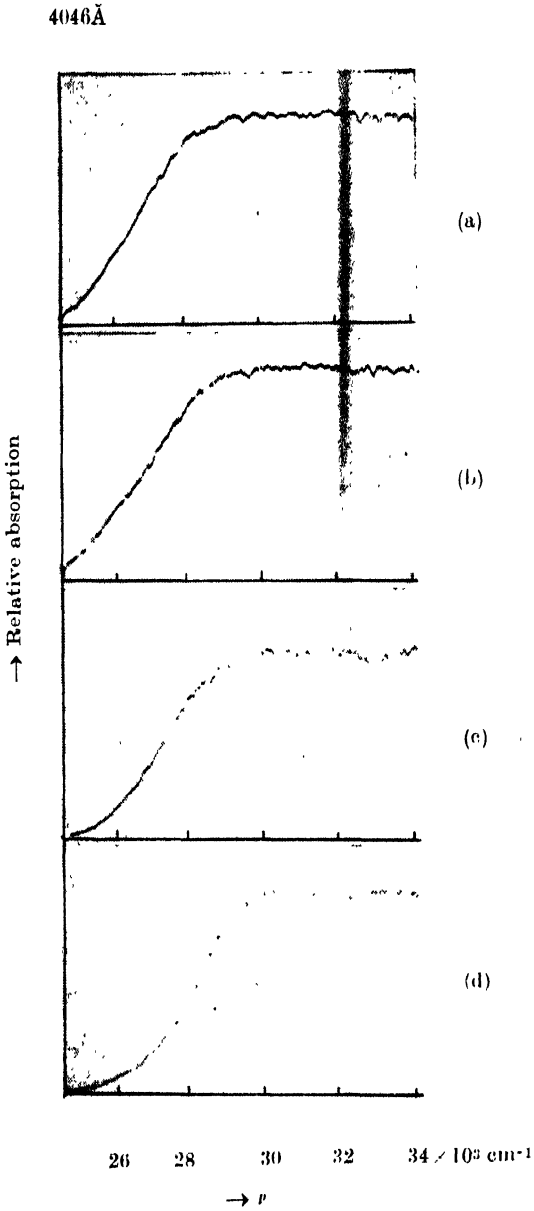

Fig. 3 (a) *m*-Fluorotoluene (liquid)
(b) *m*-Fluorotoluene (vapour)
(c) *m*-Chlorotoluene (liquid)
(d) *m*-Chlorotoluene (vapour)

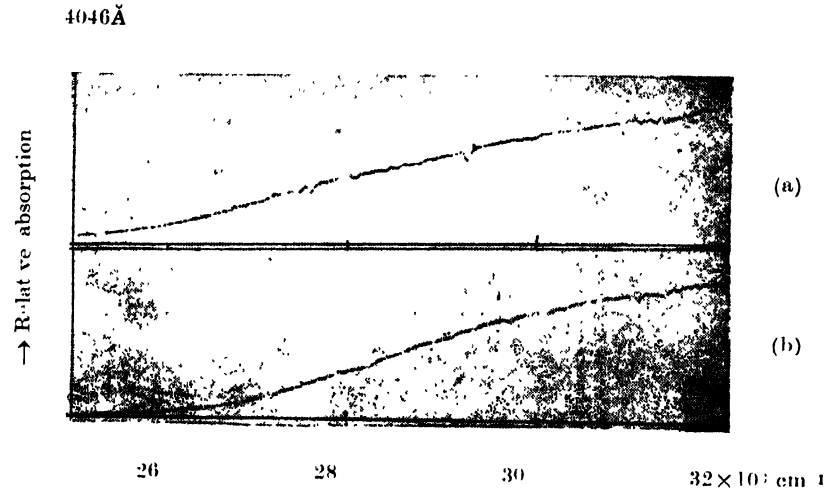

Fig. 4. (a) 2,4-Dichlorotoluene (liquid) at 30°C.
(b) 2,4-Dichlorotoluene (vapour) at 205°C

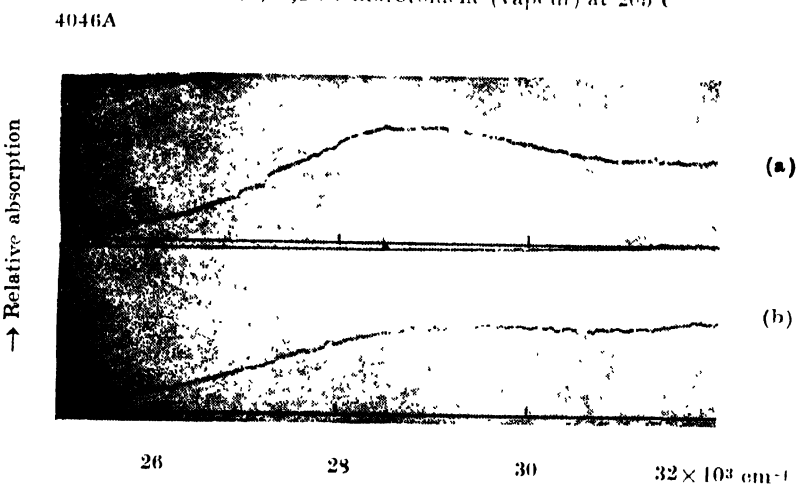

Fig. 5. (a) 3,4-Dichlorotoluene (liquid) at 30°C.
(b) 3,4-Dichlorotoluene (vapour) at 205°C

at about 30,000 cm^{-1} is larger in the case of *p*-fluorotoluene than in the case of the ortho compound, but the increase in the strength due to intermolecular field in the liquid is larger in the latter case than in the former case. Fig. 2 on the other hand shows that absorption due to the 2,4- and 3, 4-dichlorotoluene in the vapour state is almost identical in respect of position and strength, but the increase due to intermolecular field in the liquid is larger in the latter case.

It would be interesting to find out how far the strengths of absorption in the vapours of the different substituted benzene molecules can be explained with the help of vector diagrams which were used by Platt (1951) to explain the singlet→

singlet systems of such compounds. It was shown by Platt that the transition moments due to the substituents CH_3 and halogen atoms have the same sign in the case of singlet→singlet transition. Assuming this to be true for the singlet →triplet transition also, it can be seen from the vector diagrams for trisubstituted benzenes that the resultant transition moments for 2, 4-dichlorotoluene and 3, 4-dichlorotoluene are exactly the same. The curves in Figs. 2(b) and 2(d) show that the strengths of absorption and positions of the region of absorption in the vapours of the two compounds are the same. Again, the vector diagrams for disubstituted benzenes show that the transition moment of the para substituted compound should be larger than that of the ortho substituted compound. The curves in Figs. 1(b) and 1(d) show that the experimental results agree with those deduced from the vector diagrams. Figs. 3(b) and 3(d) also show that the heavier atom chlorine produces a larger transition moment than the lighter substituent atom fluorine both situated at the meta position.

It appears from these results that the substituent atoms make the forbidden transition to the triplet state allowed, but the upper triplet state becomes very broad and diffuse. Probably the perturbation due to the substituent atoms changes the nature of coupling between the spin and orbital angular momentum so that the resultant spin is not quantised and this may explain the continuous nature of the upper state.

It can be seen from the curves reproduced in all the figures that the region of absorption shifts towards longer wavelengths as the vapour is liquefied, the shift being different for the different compounds. It is remarkable, however that the long wavelength limits for the curves due to isomeric molecules with the same substituents are exactly the same. This shows that the perturbation due to the heavy substituent atom in the neighbouring molecule is responsible for the shift of the spectrum. As this effect is exhibited mostly by polar molecules it may not be unlikely that formation of loose dimers takes place in the liquid state and the shift may be partly due to such bond-formation.

Fig. 4 shows that curves due to 2, 4-dichlorotoluene in the vapour state at 205°C and in the liquid state at 30°C. A comparison of the curve due to the vapour at 205°C, Fig. 4(b) with that due to the vapour at 30°C reproduced in Fig. 2(b) shows that the curves are identical. This shows that temperature and pressure have very little influence on the absorption.

The microphotometric records of the spectra due to 3,4-dichloro-toluene in the liquid state at 30°C and in the vapour state at 205°C photographed with the high dispersion spectrograph and reproduced in Fig. 5 show that in both the curves there is a tendency for the formation of a very broad maximum. The centre of the maximum is at about 29200 cm^{-1} in the case of the vapour. The maximum is more prominent in the case of the liquid and its centre shifts to about 28500 cm^{-1}. Such a phenomenon is not exhibited by 2 ,4-dichlorotoluene. This may

be due to overlapping of the singlet→triplet and singlet→singlet systems in the latter case.

It is thus evident from the results for the compounds mentioned above that the absorption due to singlet→triplet transition is continuous with a maximum in some cases and the perturbation due to heavy atoms in the neighbouring molecules always shifts the region of absorption towards longer wavelengths.

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